Enhanced CAH Bioremediation with Soluble Carbohydrates (Molasses, Corn Syrup and Whey)

Case Study, Protocol, Current State of Practice and Federal Applications

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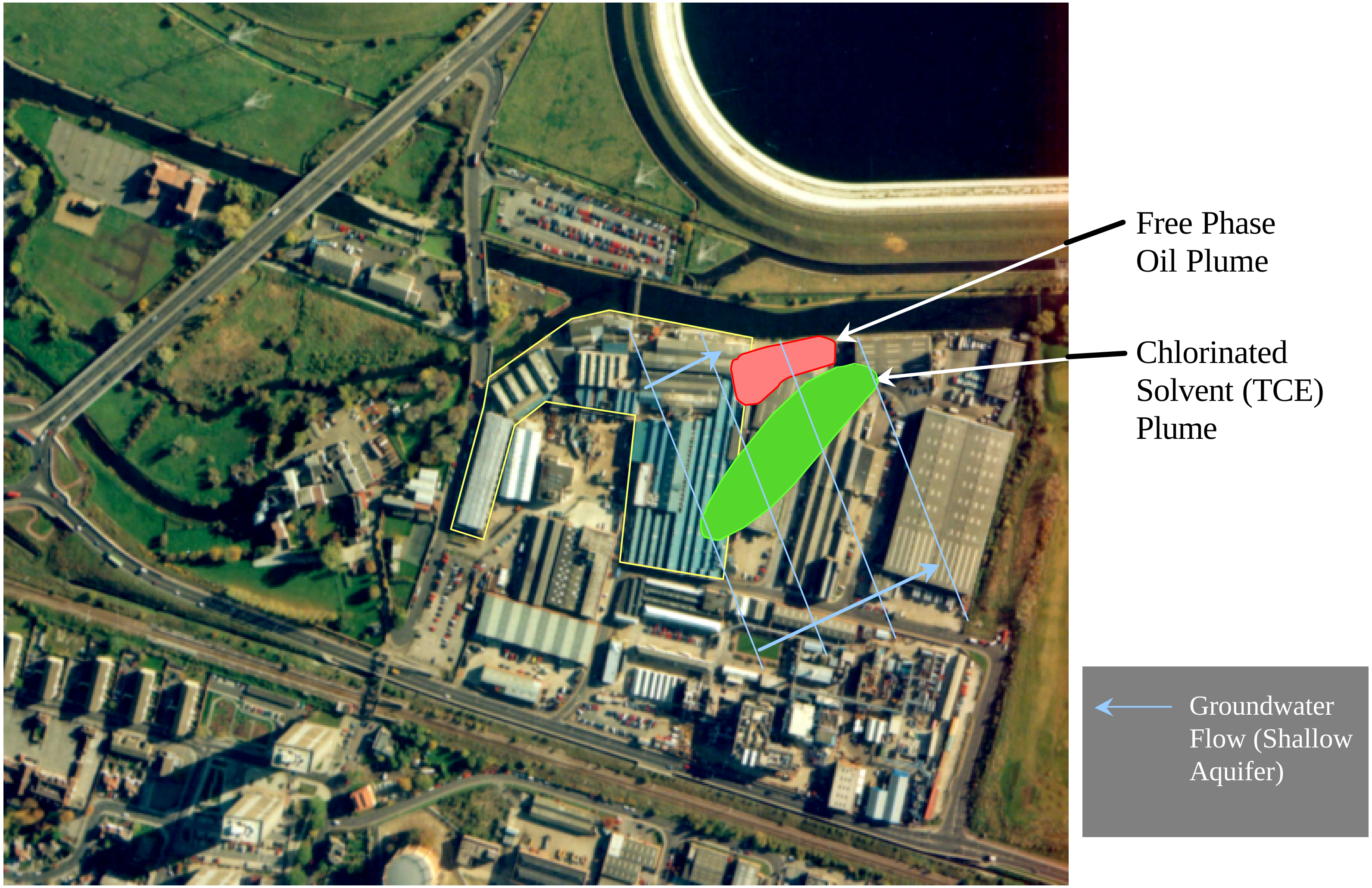
IRZ Technology

- In-situ Reactive Zone (IRZ) technology enhances natural processes in groundwater to drive conditions to a state more conducive to the degradation of a contaminant, and includes enhanced reductive dechlorination (ERD)
- With ERD, a carbohydrate solution acts as an electron donor to transform aerobic or mildly anoxic aquifers to highly anaerobic reactive zones, creating conditions for reductive dechlorination of CAHs

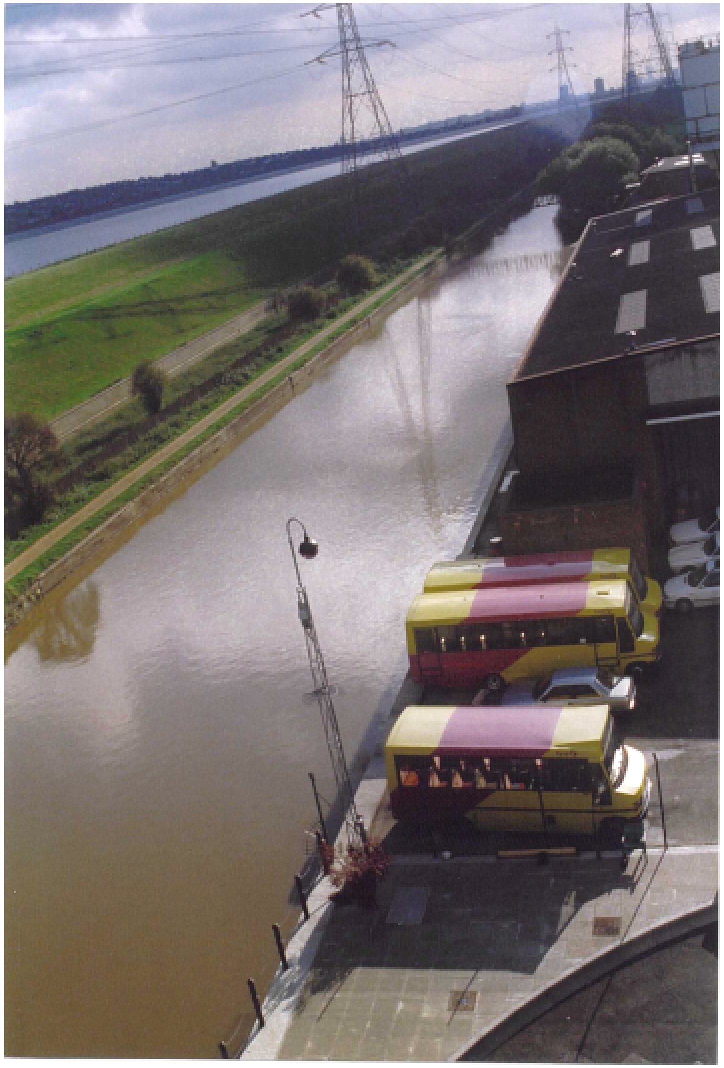
Case Study: TCE Plume in SE England

- **Manufacturing facility**
- **CAH plume underlying planned building expansion**
- **22 mg/L TCE**
- **Sand and gravel aquifer, 12 ft thick, 20 ft bgs, over a clay aquitard**
- **K = 0.1 - 0.01 cm/s, v_x = 86 - 865 cm/day (2 - 28 ft/day)**
- **Baseline – nitrate to iron-reducing conditions below building, with incomplete dechlorination. Anaerobic, reducing conditions downgradient where commingled with petroleum hydrocarbon plume**

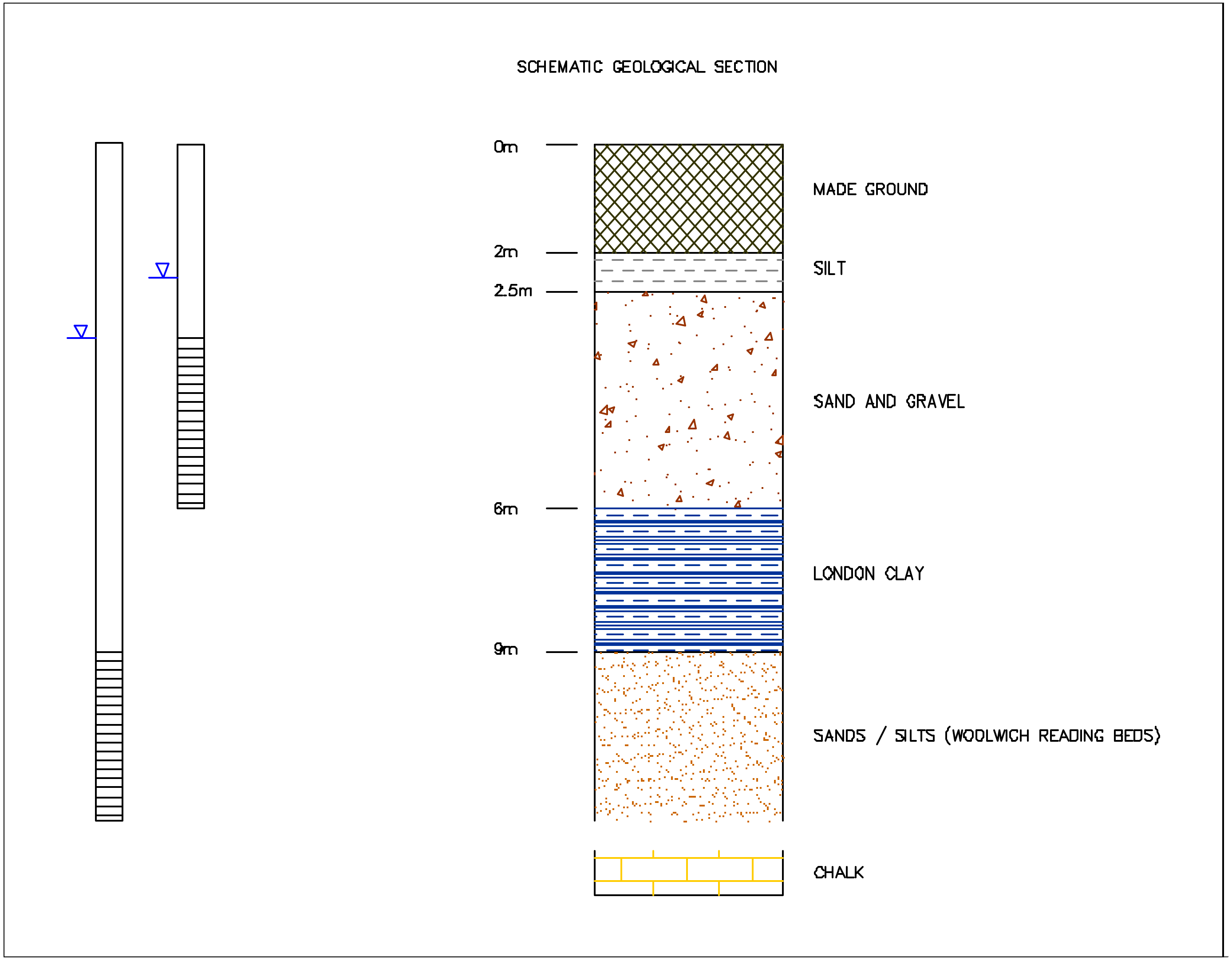
Site and Contaminant Plumes



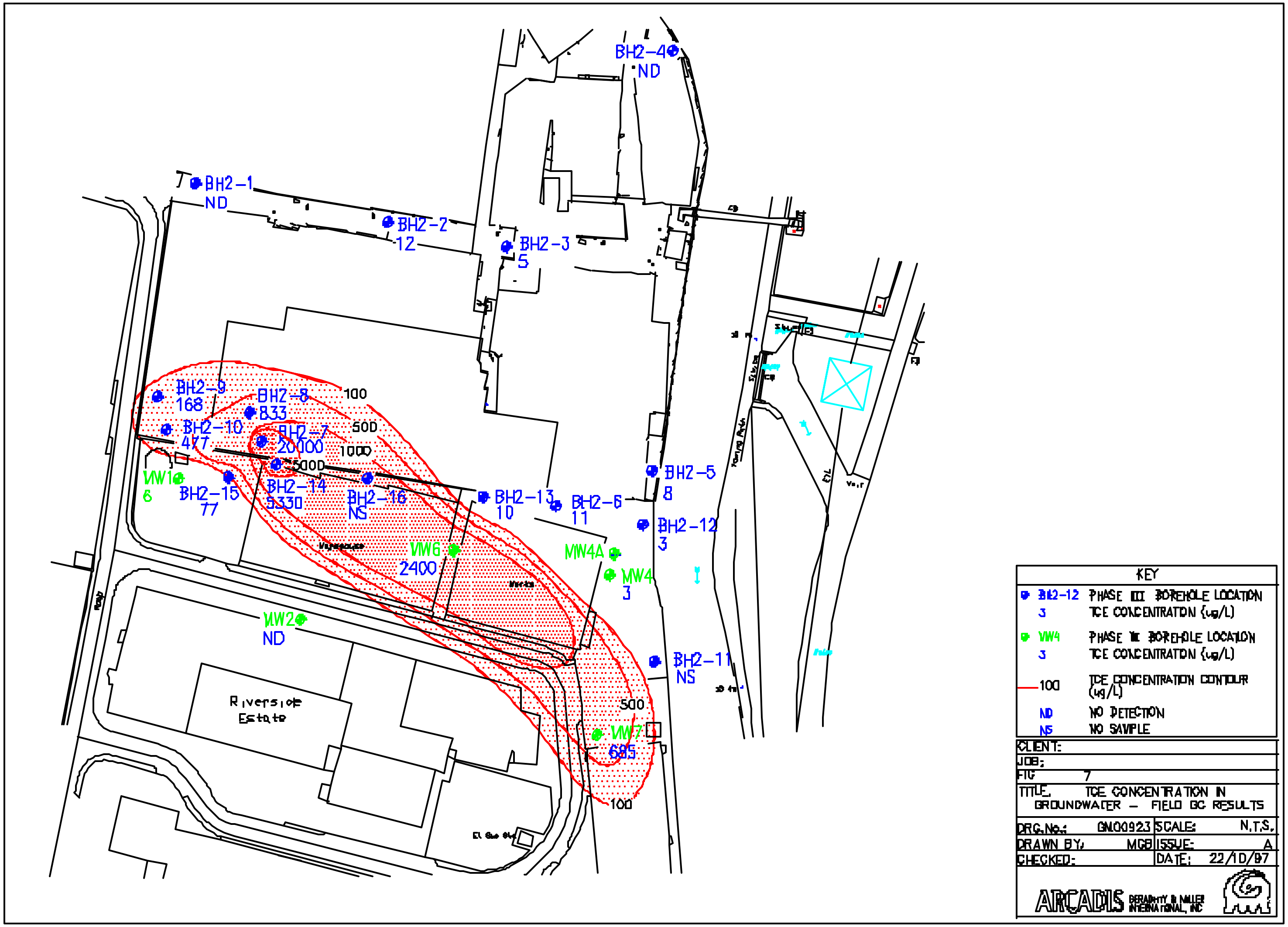
River at Toe of Plume



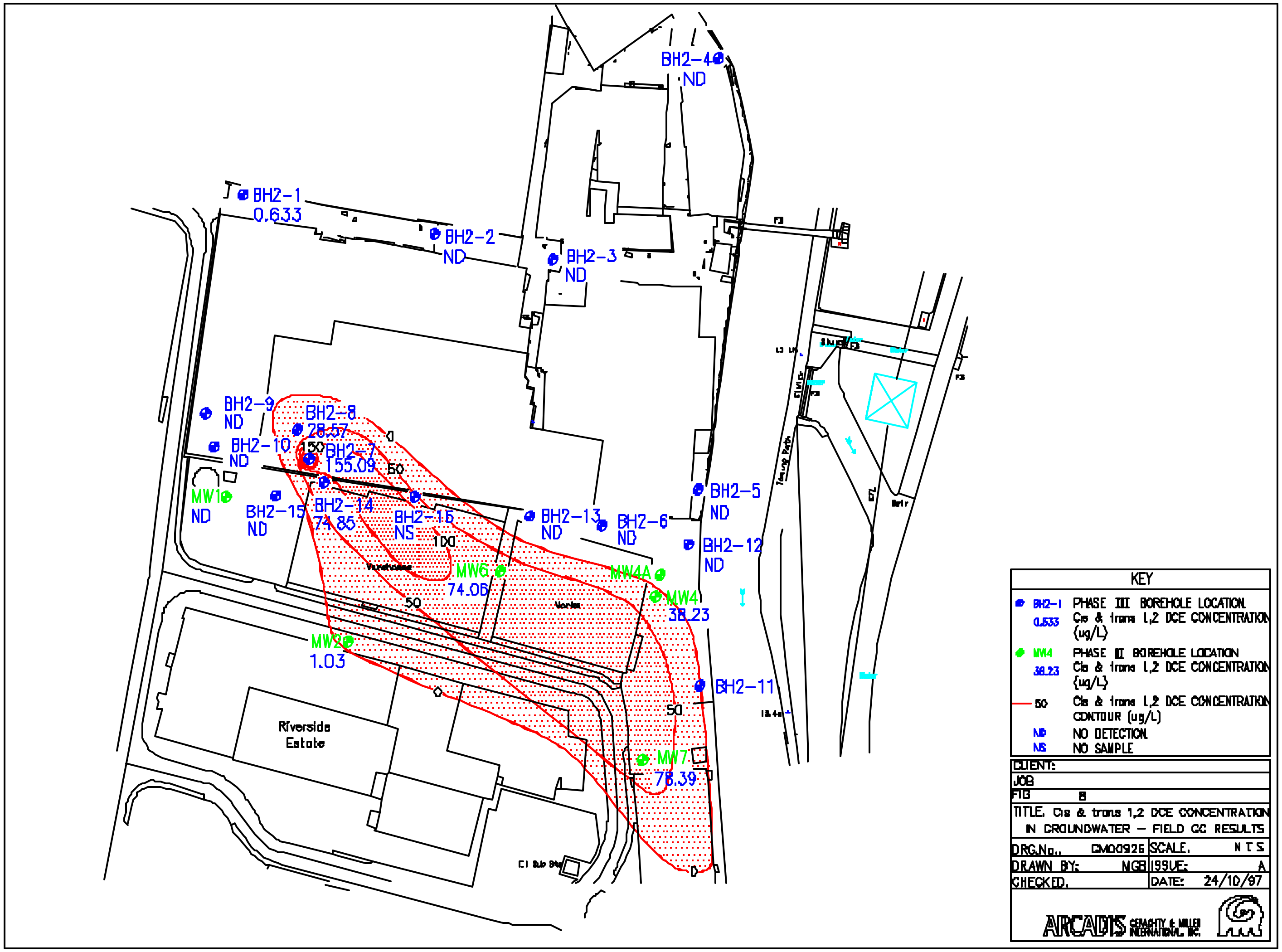
Geology


SCHEMATIC GEOLOGICAL SECTION
0m
2m
2.5m
6m
9m
MADE GROUND
SILT
SAND AND GRAVEL
LONDON CLAY
SANDS / SILTS (WOOLWICH READING BEDS)
CHALK

Initial TCE Distribution



Initial 1,2-DCE Distribution



Remediation Design Challenges

- 22 mg/L TCE
- Integration of remediation system into construction of a building expansion
- Groundwater velocities 2 to 28 ft/day (exceeding recommended 0.08 to 5 ft/day for ERD)
- Control of by-products - primary exposure pathway is vapor intrusion into building (based on air modeling and risk assessment). Potential by-products of ERD were CH_4, H_2S, VC

Design Parameters

- Two rows of injection wells installed in trenches built into slab of new building
- 53 Injection wells on ~10 ft centers
- 6 Vapor extraction wells and a vapor membrane below building
- Automated reagent injection distribution system installed on roof of new building

Rooftop Reagent Injection System

Reagent Injection System

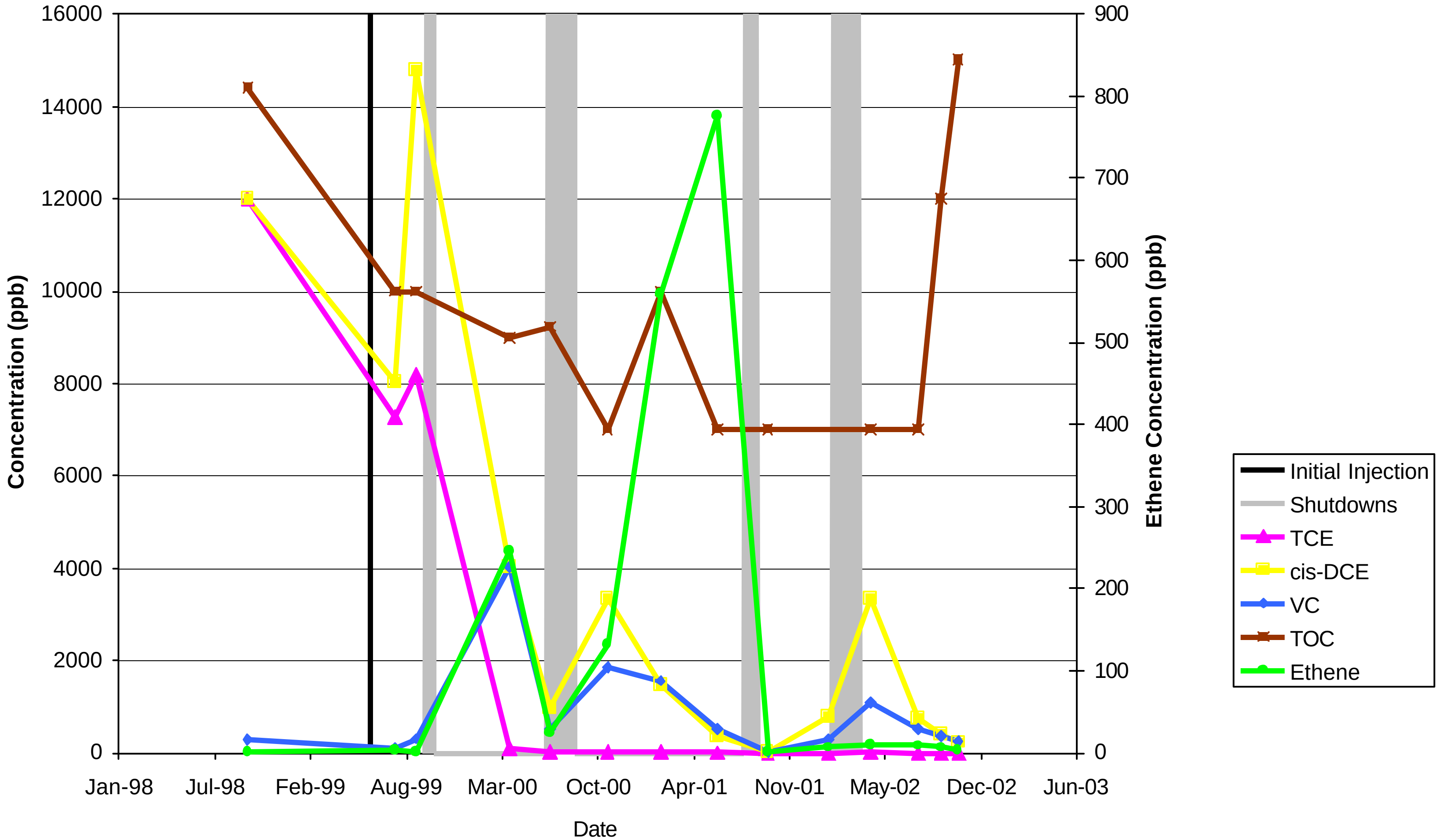
Operational Parameters

- Started cautiously – Low-strength reagent (water to molasses ratio 50:1) and used only 10 of 53 injection wells
- System operates on a 24-hr cycle with injections between 10 a.m. and 6 p.m.
- Initially injected 21 lbs of organic carbon/day
- After 2 years, increased dosing strength and volume to 57 lbs organic carbon/day

Operational Parameters (cont'd)

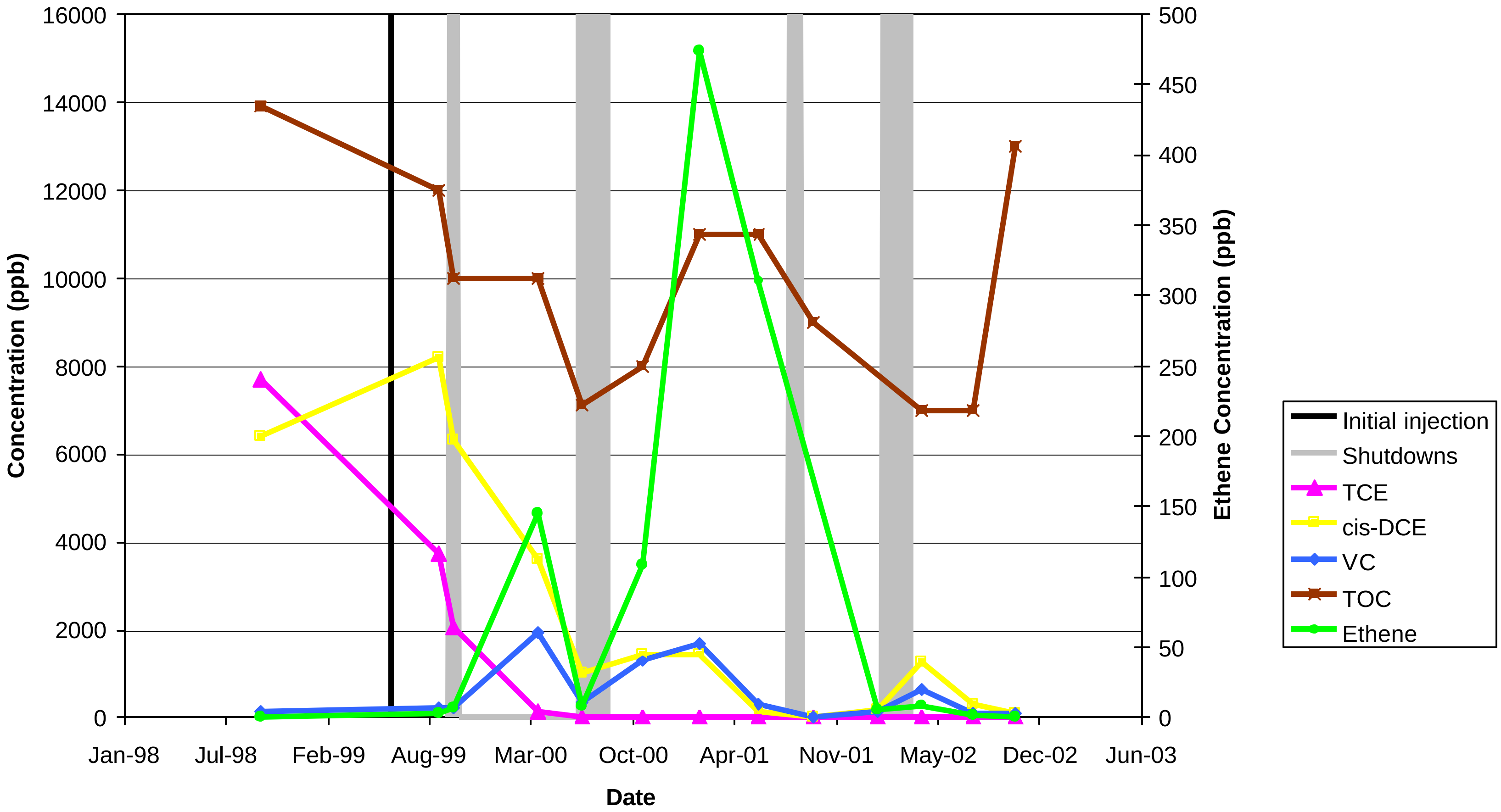
- 15,000 lbs organic carbon delivered in first two years
- Molasses chosen for its low cost - $0.20/lb of organic carbon
- Reagent costs a relatively small portion of O&M cost

Groundwater Chemistry Data



Downgradient Well MW-5, Southeast England Site

Groundwater Chemistry Data



Downgradient Well MW-6, Southeast England Site

Case Study Conclusions

After 2 years of monitoring:

- TCE reduced from 22 mg/L to 0.014 mg/L
- Cis-DCE increased from 12 mg/L to 21 mg/L
- VC increased from 0.3 to 4.5 mg/L
- Ethene increased from 0.002 to 1.5 mg/L, indicating complete dechlorination

TOC dosing has been boosted to increase rates of treatment for cis-DCE and VC

Case Study Conclusions (cont'd)

After 2 years of monitoring:

- **Reducing environment enhanced, as indicated by**
  - **Lower DO, nitrate, sulfate levels**
  - **Increased iron levels**
- **TOC levels similar to baseline!**
  - **Volume of substrate used is large because high v_x = large volumes of water to treat**
  - **TCE reductions achieved without the relatively high TOC levels employed at most ERD sites**
  - **Prevented undesirable fermentation, by-product formation**

Case Study Conclusions (cont'd)

Other Challenges Met:

- **High frequency & volume of substrate addition used to overcome high velocity**
- **Success in integrating system with building design and construction**
- **Prevented accumulations of vapors in building**

ARCADIS' General Approach to ERD as Outlined in Protocol

- **Bioaugmentation is rarely needed**
- **Co-metabolic and dehalorespiring processes work together in real world systems**
- **Buffers can be a big help in avoiding too much fermentation**
- **Suppression of hydrogen levels is unnecessary and may inhibit full dechlorination**

ARCADIS' General Approach to ERD as Outlined in Protocol

- Desorption processes are critical to the performance of these systems
- Microcosms are rarely needed but "tuning" the field pilot system is vital
- The highest treatment efficiencies are associated with high TOC and often with methanogenic conditions

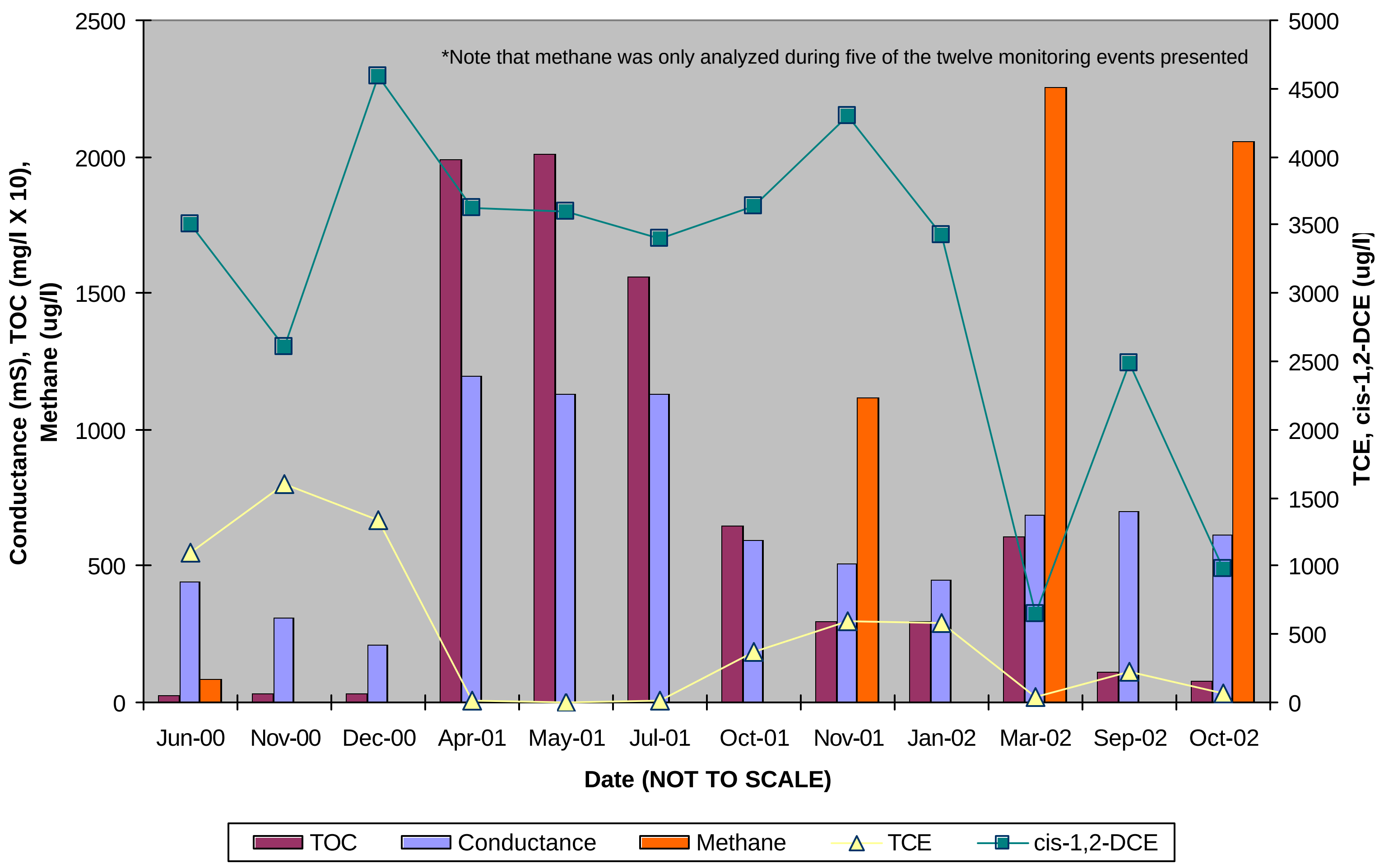
Baseline Site Information

Pretreatment CAH Concentrations (ug/L)	Depth to GW (ft bls)	K_x (ft/day)	v_x (ft/day)	Gradient (ft/ft)	Depth of Treatment Zone (ft bls)
TCE 810-1900 1,2-DCE 1600-5300 VC 360-1300 1,1-DCA 100-170	4 – 8	26 (typical)	0.8	0.006 (typical)	50

Baseline Geochemistry (min/max)

DO (mg/L)	ORP (mV)	PH (su)	Nitrate (mg/L)	Sulfate (mg/L)	Sulfide (mg/L)	CO_2 (mg/L)	Methane (ug/L)
0.35/1.48	-57.5/200	5.73/7.10	ND	21.5/38.9	ND/0.1	9.4/86.2	15/138.8

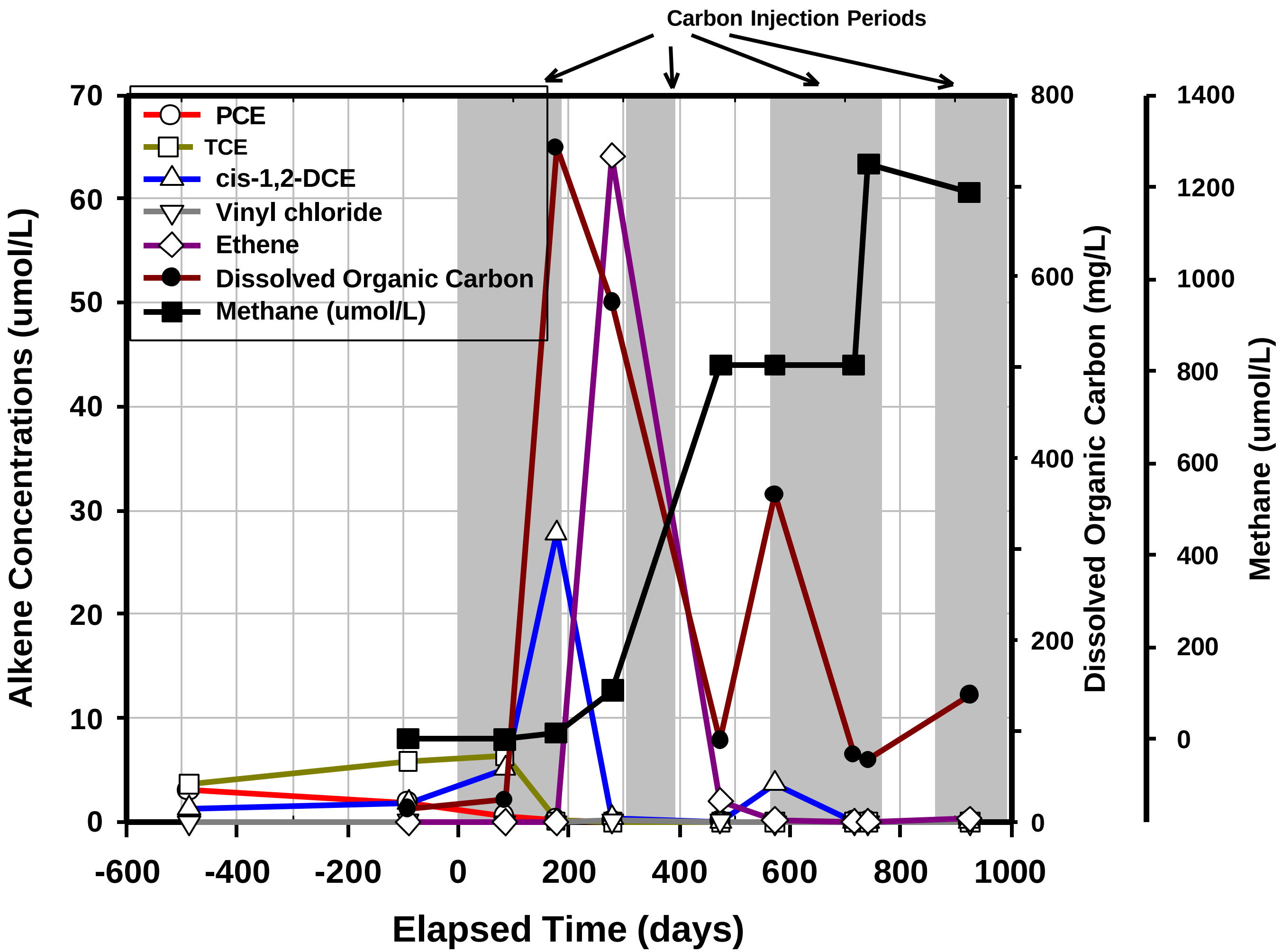
Hanscom: IRZ-1 COC Response to Reagent Delivery



Southwest Ohio Commercial ERD Site

- ERD reactive barrier operated for 2.5 years to date
- Influent concentrations 500 µg/L PCE, 700 µg/L TCE
- Groundwater velocity 1 ft/day
- Monitoring location 100 days downgradient from barrier

Long-Term Operation of ERD at Southwest Ohio Site



Summary of ARCADIS Experience

- **ARCADIS has been involved with more than 140 IRZ sites, across five countries and 26 U.S. states**
- **Twenty-six sites are full-scale implementations; three have achieved closure**
- **Additional sites are ongoing pilot applications, or Interim Remedial Measures, or are completed pilot projects that are now in the full-scale design phase**

Experience and Technology Transfer (Cont'd)

The technology has successfully been applied to the following chlorinated compounds and metals

- TCE, DCE, VC, CT, chloroform, chlorinated propanes, pentachlorphenol (PCP), pesticides, trichlorofluoromethane, and perchlorate
- Hexavalent chromium, nickel, lead, cadmium, mercury, and uranium

ARCADIS ERD at DoD and DoE Sites

- Hanscom AFB, MA – AFCEE/ESTCP demonstration recently completed
- Vandenberg AFB, CA - AFCEE/ESTCP demonstration underway
- Fort Devens, MA – Field pilot under GFPR contract
- Naval Weapons Industrial Reserve Plant, Dallas, TX – pilot completed
- Lompoc Federal Penitentiary, CA – pilots pending at two sites under GFPR contract

ARCADIS ERD at DoD and DoE Sites (Cont’d)

- Fernald Environmental Management Project – bench scale for uranium underway under contract with NETL
- Fort Leavenworth, KS – Planned applications at two sites under GFPR contract
- Charleston AFB, SC – planned application under guaranteed fixed price AFCEE ENRAC task order
- Milan Army Ammunition Plant, TN – demonstration for energetics contracted through AEC/Plexus
- Fort Ord, CA – pilot at OU-1 for TCE, Sacramento AEC/ by subcontract to AGSC

Protocol Content

Site Selection for Enhanced Anaerobic Bioremediation of CAHs and/or Metals

- Site must be at least moderately permeable ($K>10^{-4}$ cm/sec)
- We prefer sites that are reasonably well delineated geologically and with regard to contaminant concentration
- pH should be 5-9
- Presence of DNAPL or sorbed source material is not a barrier to successful implementation, but must be figured into estimated treatment time and overall treatment goals

Protocol Content (cont'd)

- **DO recharge rate and concentrations of alternate electron acceptors such as nitrate and sulfate must be factored into estimated treatment time and if extreme may make treatment less cost-effective**
- **Co-contaminants, including various chlorinated species, metals, Cr^{+6}, Ni, Pb, Cd, Zn, Hg, radionuclides like U and Tc, nitrate, and perchlorate are ok**
- **We prefer aerobic or borderline aerobic/anaerobic starting conditions. Sites that already show some breakdown products are ideal**

Protocol Content - System Modifications to Deal with Special Site Conditions

Condition	Modification
Low pH or low buffering capacity	Use of buffer Use of water push Use of slower-release substrate.
Low permeability/velocity	Closely spaced direct push injections made less frequently
Salinity	Low sulfate donor (e.g., corn syrup) Larger TOC dose
Buildings above reactive zone	Gas monitoring systems Gas control systems

Protocol Content - Delivery System Design

- Delivery systems can range from complex/automated to low cost/mobile
- Injection frequency can vary from weekly to semi-annual
- In-depth hydrogeological understanding is key – pump tests can be useful, seasonal effects on water table and velocity must be considered
- No design will be perfect – all systems require several months of monitoring and adjustment in the field

Protocol Content – Carbon Substrate Selection

- **Substrate must be matched to hydrogeology and biogeochemistry**
- **Key factors include size of site, desired treatment time, velocity, oxygen recharge rate, and concentration of alternate electron acceptors**
- **Substrates range from rapidly consumed to slowly released**

Protocol Content - Carbon Substrate Selection (Cont'd)

- **Substrates' physical and biological characteristics influence injection system design**
- **Key is to couple the right substrate with the right injection system design**
- **ARCADIS has successfully applied molasses, whey, and corn syrup**

Summary of Technology Application Costs

Site	Estimated Capital Costs	Estimated Annual O&M Costs	Actual or Predicted Costs to Closure
Industrial Laundry/Dry Cleaning Facility, Eastern PA	$ 75,000	$ 45,000	$ 250,000
Uranium Processing Facility, Eastern US	$ 480,000	$ 65,000	$ 760,000
Former Metal Plating Site, Western US *	$ 100,000	$ 150,000	$ 250,000
Industrial Manufacturing Site, South Carolina	$ 1,400,000	$ 75,000	$ 2,000,000
Industrial Site, Northeastern US	$ 150,000	$ 80,000	$ 750,000
Former Dry Cleaner, Wisconsin *	$ 200,000	$ 100,000	$ 400,000
Former Automotive Manufacturing Site, Midwestern, US	$ 75,000	$ 60,000	$ 375,000
AOC 50, Ft. Devens, Ayer, Massachusetts	$ 150,000	$ 150,000	NA[1]

Note:
Costs presented in current dollars.
* Site has received regulatory closure.
[1] No predicted costs to closure available. Pilot study ongoing.